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Characterization of precious opals: AFM and SEM observations, photonic band gap, and incorporation of CdS nano-particles

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Abstract

Gem-quality blue opals consisting of ≈ 200 nm silica spheres are synthesized and incorporated with CdS nano-particles by a solution technique. The opals with and without CdS are characterized by atomic force microscopy, scanning electron microscopy and conventional optical spectroscopic measurements. The possibility of producing 3-dimensional arrays of nano-sized materials and photonic crystals is supported by these experiments.

Keywords: Synthetic opal; Cadmium sulfide; Atomic force microscopy; Scanning electron microscopy; Photonic band gap

1. Introduction

Opals consist of close-packed silica spheres of nearly equal sizes [1]. Diameters of spheres can vary in the range 100–500 nm, depending on methods of preparation. Spaces between spheres form voids of two types: tetrahedral cavities (small ones) and octahedral cavities (large ones) [1,2]. Since the spheres are regularly arranged with suitable lattice parameters, the whole array should act as a 3-dimensional (3-D) optical diffraction grating. This property gives to opals their value as jewelry. Recent scientific interest in opals is associated with a number of possible applications in optics, electronics and solid state physics [2–5]. Since

opals are 3-D periodic structures of the order of visible wavelength, they can be realized as photonic band gap materials for the visible light region [3,4]. Moreover, they can be used as matrices for the fabrication of the regular arrays of nano-sized systems in the voids between the spheres, giving rise to a solid state with new electric, dielectric and optical properties [2,4,5]. 3-D arrays of semiconducting nano-particles are especially interesting for these purposes. Realization of these ideas needs elaboration of the methods of the opal synthesis and incorporation of semiconducting materials into the opal voids, detailed information about the structure of opals and incorporated materials being very important.

In the present work, gem-quality opals have been synthesized. The opal samples both without

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and with incorporated CdS nano-particles have been characterized by atomic force microscopy (AFM) for the first time. The AFM method can achieve high resolutions in three dimensional topography on both conductors and insulators. It can be used in ambient conditions and allows observations without any special surface treatment such as metallic coating which is necessary for scanning electron microscopic measurements. Results of AFM characterization have been supplemented with observations by scanning electron microscopy (SEM), as well as with measurements by conventional optical methods. The photonic band gap of the investigated opal has been studied.

2. Experimental

Synthetic gem-quality opals prepared by a similar method to that described previously [6–9] were used in our experiments. First, mono-dispersed suspensions of spherical particles of amorphous silica were synthesized with dimensions in the range 150–250 nm. The opalescent solid was precipitated by sedimentation or centrifugation of the suspensions. Finally, it was heated in order for the spheres to adhere well together. Synthesized opal showed bright blue reflections. Nanoparticles of CdS were synthesized in the opal by a solution technique of two reaction stages [10]. At the first

stage, the opal sample was immersed into a CdSO_4 solution with Cd^{2+} ions of 0.1 M concentration for 10 min at room temperature, and then rinsed and dried. At the second stage, the sample was sulfurized in a Na_2S solution with S^{2-} ions of 1 M for 3 min at room temperature. Formation of CdS has been controlled visually by observation of a yellow color of the opal sample and by observation of characteristic CdS Raman bands.

AFM measurements were performed with NanoScope II (Digital Instruments Inc.) in air at room temperature. Standard silicon nitride tips on the 200 micron triangular cantilever with a spring constant of 0.12 N/m were used. SEM measurements were made on a high resolution scanning electron microscope (S-4100L, Hitachi Co.). Because this sample has a poor conductivity, it has been coated with Pt film (2–3 nm thick) by the ion sputtering method. Raman spectra of the sample were measured in air with the 488 nm line of an Ar^+ ion laser. The optical transmission spectrum of the pure opal has been measured on the plate parallel to the {111} plane of the crystal using a micro-spectrophotometer with a light-probe size of $\approx 50 \mu\text{m}$.

3. Results and discussion

Fig. 1 shows a typical AFM image in the constant height mode of an as-prepared opal sample

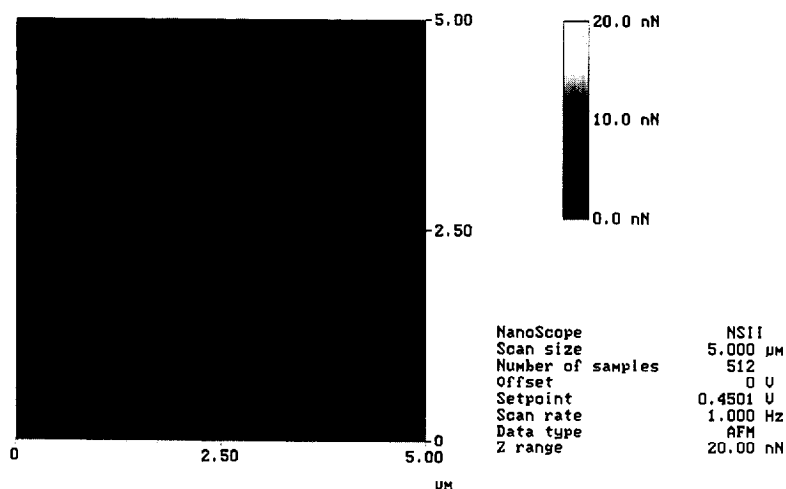


Fig. 1. AFM image in the constant height mode of a pure opal surface in the scan area of $5 \times 5 \text{ nm}^2$.

with the surface parallel to the $\{111\}$ plane. It exhibits some orderings of nearly mono-sized silica spheres of ≈ 200 nm in diameter in a close-packed structure at the surface layer. Silica spheres in opals are usually stacked randomly, but often exhibit parallel domains of commonly fcc but sometimes hcp [11]. The opal forms voids either in the tetrahedral or octahedral sites. These voids are connected together in different geometries depending on stacking disorders. There exist several irregularities associated with vacancies and local orders. Some of them may be related to twins, stacking faults and polytypism [11,12].

Figs. 2A and B display magnified AFM images in the constant force mode of the same sample and its 3-D representation, respectively. They show more clear images of individual silica spheres. It is seen that the spheres display a porous structure. Fig. 3 shows a 40° tilted SEM image of a pure opal coated with Pt. This image shows that each silica sphere consists of SiO_2 micro-crystals 10–20 nm in diameter.

The optical transmission spectrum of the opal sample immersed in distilled water is shown in Fig. 4. The measurements have been made for the light beam parallel to the $\langle 111 \rangle$ direction of the

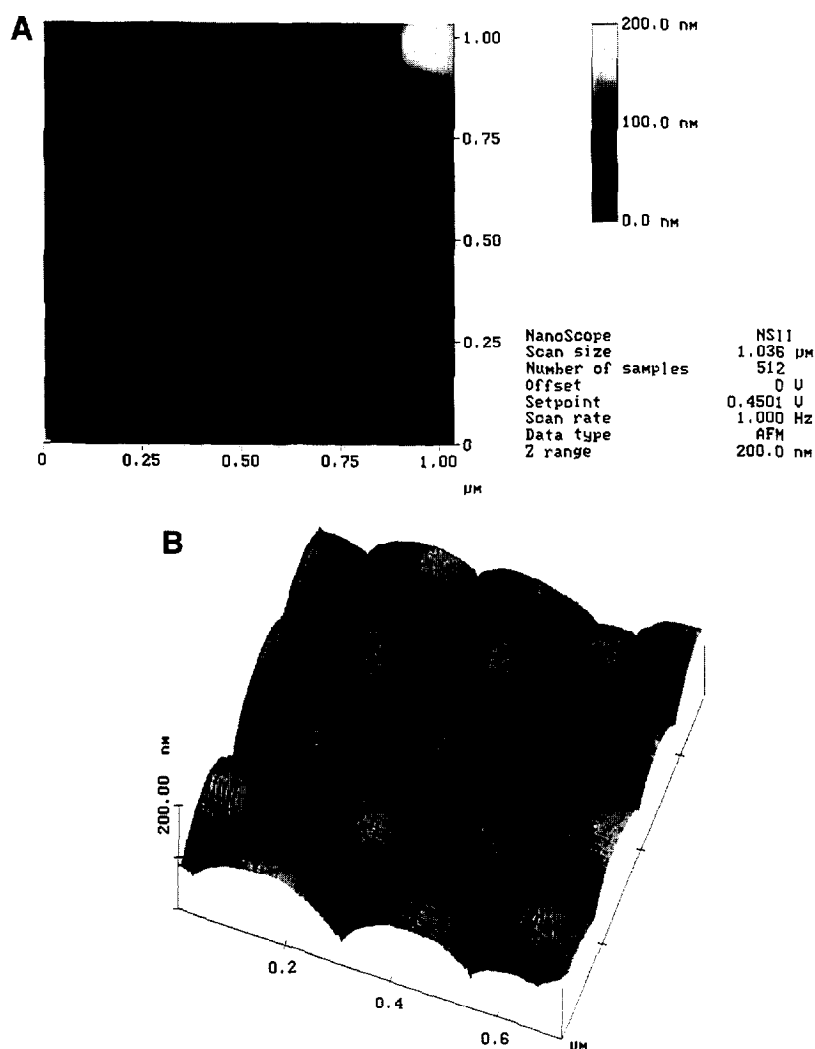


Fig. 2. (A) Magnified AFM image of the same sample shown in Fig. 1 and (B) its 3-D representation.

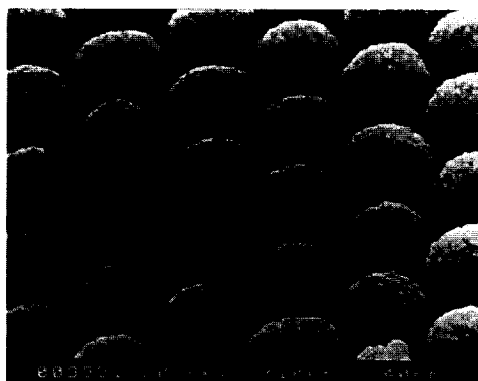


Fig. 3. 40° tilted SEM image of a pure opal.

opal lattice. A pronounced drop in transmission is observed at the light wavelength $\lambda \cong 470$ nm (photon energy 2.64 eV). This feature is displayed due to the Bragg's reflection condition, similar to that well-known for X-ray reflections from the atomic layers of crystals. From the Bragg relationship with the Bragg angle $\theta = \pi/2$ and the refraction index $\mu = 1.41$ (an average index between water and fcc silica), we can estimate the distance between the (111) planes $d = \lambda / (2\mu) \cong 167$ nm. For the fcc optical lattice, the lattice parameter $a = \sqrt{3}d \cong 289$ nm, and the diameters of the opal spheres $R = a\sqrt{2}/2 \cong 204$ nm. This value is nearly equal to the diameters of opal spheres observed by AFM and SEM. Using the photonic band gap terms [13], we can say that the gap is centered at ≈ 2.64 eV for the L-point of the fcc Brillouin zone in reciprocal space.

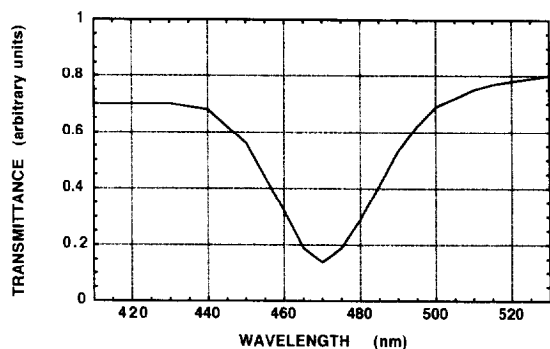


Fig. 4. Transmission spectrum of a pure opal plate immersed in distilled water.

The synthesis of CdS particles in the opal voids has been examined by resonance Raman scattering. Fig. 5 shows an unpolarized Raman spectrum of the opal sample with CdS particles. This measurement confirms the presence of CdS micro-crystals in our samples. The Raman shifts of the observed bands 302 cm^{-1} and 600 cm^{-1} are close to those of the LO-phonon of the bulk CdS crystal 305 cm^{-1} [14] and its overtone. The frequency 302 cm^{-1} is characteristic for CdS precipitated from the mixture of CdSO_4 and Na_2S water solutions. A small red-shift of the dominant Raman band from 305 cm^{-1} to 302 cm^{-1} is too weak to be attributed to the exhibition of the surface phonon of a single CdS particle [15,16]. Size effects including structural phase transitions in CdS and/or some structural tensions can be also responsible for the 3 cm^{-1} frequency shift observed here.

Fig. 6 shows an AFM image in the constant force mode of the opal incorporated with CdS. It displays CdS nano-particles in the space between three nearest neighbor silica spheres. Fig. 7 shows a cross-section analysis of the sample surface of opal with CdS. It displays that the height difference from the top of a sphere is 14 nm to that of a CdS particle, 28 nm to the center of a valley between two nearest neighbor opal spheres and 42 nm to the center of a well surrounded by the three nearest neighbor spheres. These values are found to be similar over the sample surface, indicating that each CdS particle occupies each void in a similar manner.

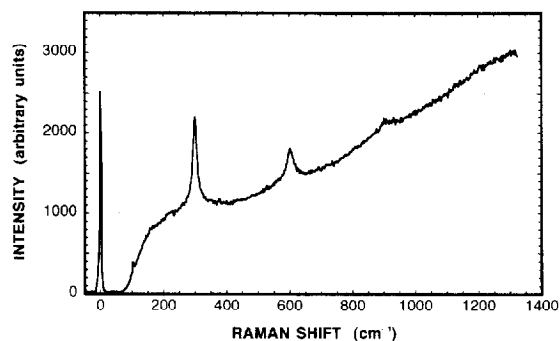


Fig. 5. Unpolarized Raman spectrum of an opal containing CdS nano-particles measured with the 488 nm line of an Ar^+ ion laser. The sharp decrease of intensity below 180 cm^{-1} is due to the 488 nm notch filter used in our measurement.

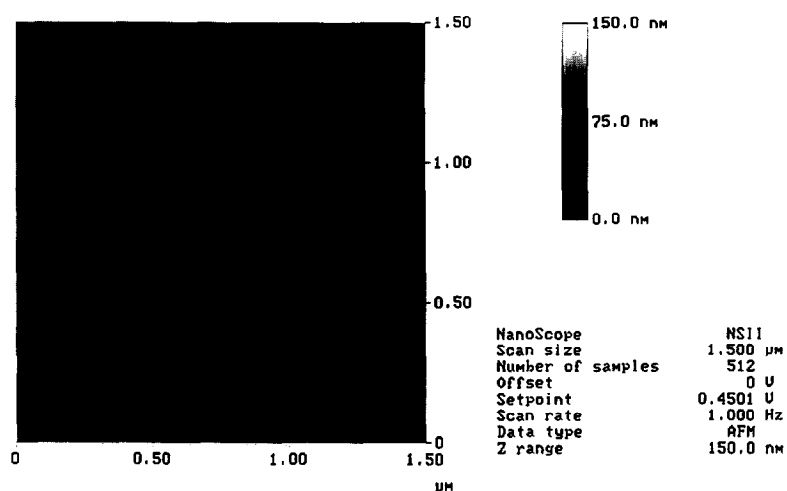


Fig. 6. AFM image in the constant force mode of an opal surface incorporated with CdS. The scan area is $1.5 \times 1.5 \text{ nm}^2$.

Close examination of Figs. 6 and 7 reveals that the CdS particles do not occupy every space between the three spheres, due to their small

concentration. The occupancy was evaluated to be less than 33% in Fig. 3. The chemical method used in the present work is expected to yield a low

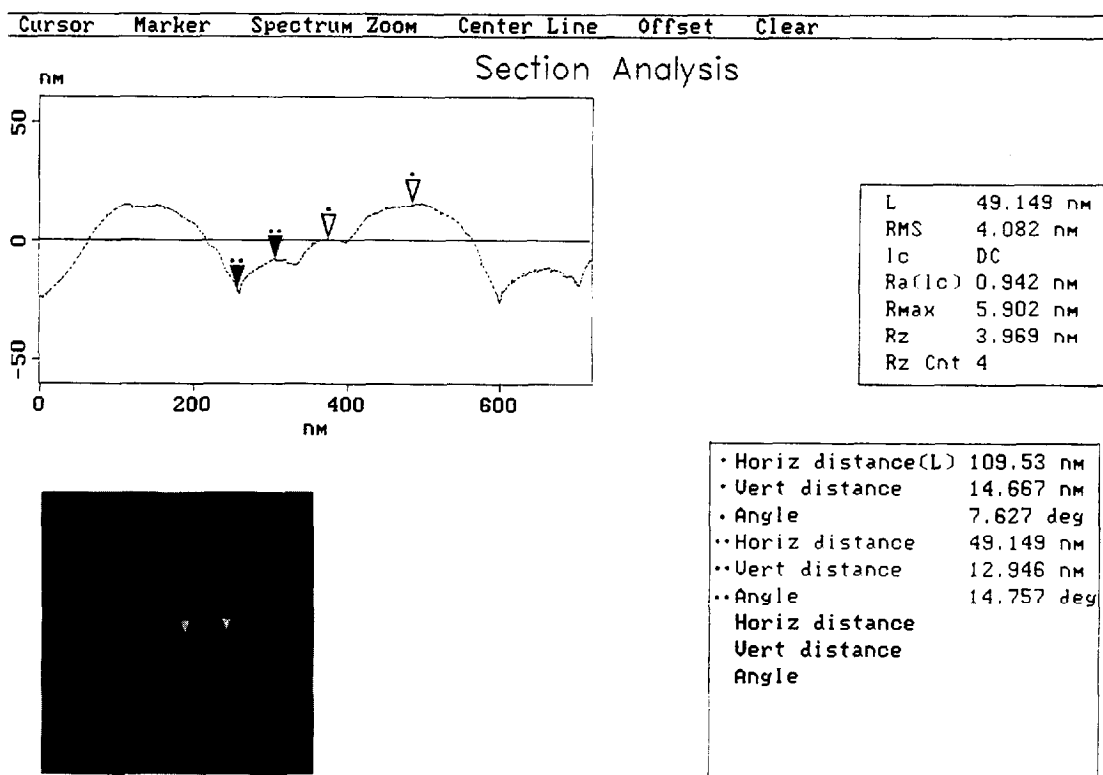


Fig. 7. Cross-section analysis of the AFM image shown in Fig. 6.

concentration of CdS particles because of their slow diffusion through and low wetness on silica spheres. The chemical reaction was controlled to take place slowly and gently so as to minimize possible damage on the surface of opal for AFM observations. The concentration could be made higher, but the sample prepared with more concentrated solutions, e.g. 0.2 M of Cd^{2+} and 2 M of S^{2-} , shows a surface mainly covered with excess CdS precipitates which prevent us from measuring its details.

Figs. 8A and B show, respectively, a magnified

AFM image and its 3-D representation, where the concentration of CdS particles is higher compared with other areas on the surface. They exhibit a regularity in the arrangement of CdS particles such that for none of them are the nearest neighbor sites occupied. This result can be explained if one assumes that CdS particles cannot occupy tetrahedral sites, but only octahedral sites of close-packed spheres. Since one cannot distinguish between the above two types of sites by looking at the top of the layer only, this regularity must come from the stacking sequences below the top layer. It is easier

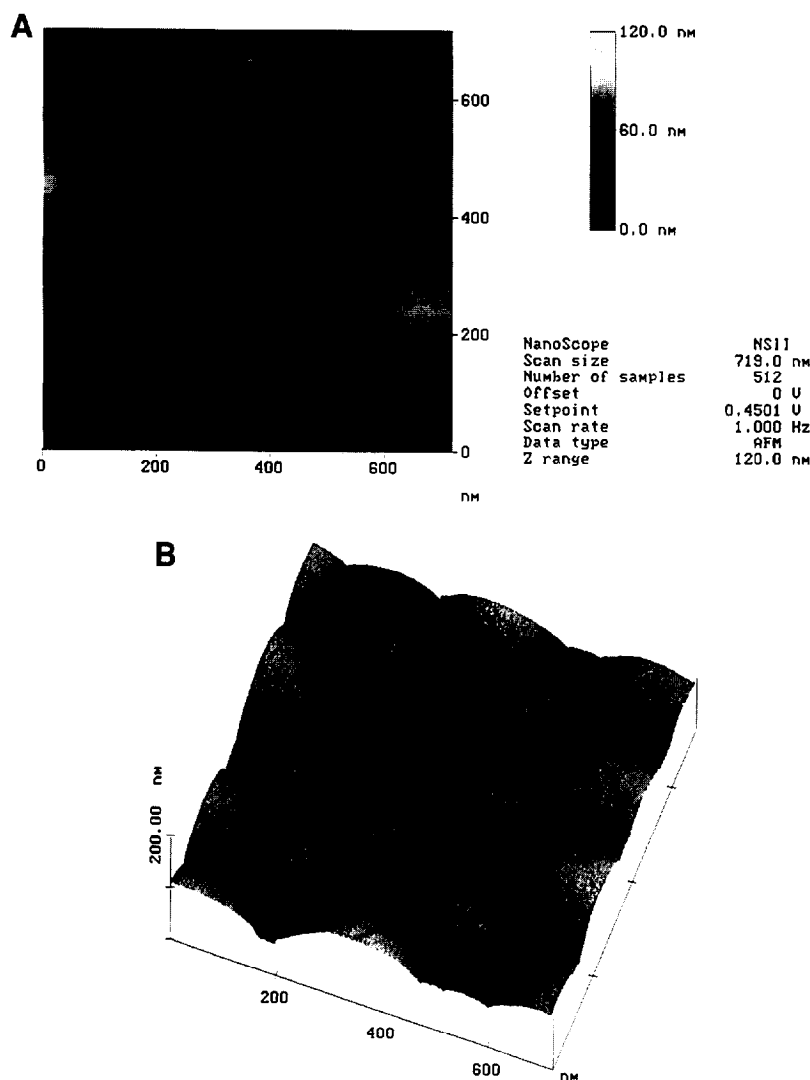


Fig. 8. (A) AFM image in the constant force mode for an opal fully incorporated with CdS and (B) its 3-D representation.

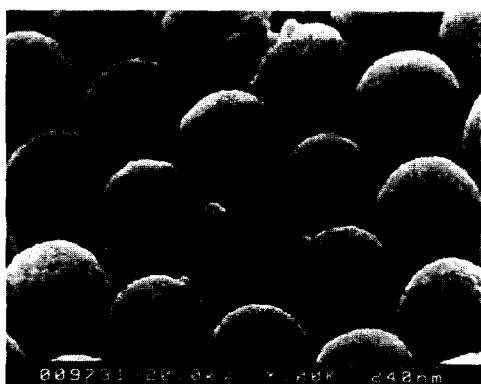


Fig. 9. 40° tilted SEM image of an opal incorporated with CdS.

for the CdS particles to be filled and stay in the space, because the octahedral site has a larger volume of empty space than the tetrahedral one. In the perfect hcp (ABAB) stacking of bulk opal, CdS particles located in (C) sites are connected together in the vertical direction throughout the sample from the top layer to the bottom. The connected CdS particles may be regarded as a quantum wire. The presence of a stacking fault terminates the connection of CdS particles. In the perfect fcc (ABCABC) stacking, CdS particles located in octahedral and/or tetrahedral sites may be regarded as a regular array of quantum dots.

The results of the AFM observation were compared with those of high resolution SEM. Fig. 9 shows a 40° tilted SEM image of the opal incorporated with CdS particles. It displays aggregations composed of CdS particles of the diameter 10–40 nm in the voids. Compared with the AFM image in Fig. 8B, the SEM image overestimates roughly two times the size of CdS particles, possibly due to the Pt coating and edge-enhancement effects.

4. Conclusion

To summarize: we have prepared a gem-quality blue opal. AFM and SEM observations of the opal show good uniformity of silica spheres with about 200 nm in diameter and good regularity of their packing in the lattice. Micro-crystalline structure (size of crystallites, 10–20 nm) of the silica

spheres has been clearly observed in SEM images. A pronounced photonic band gap of the opal immersed into distilled water has been observed at 470 nm (≈ 2.64 eV) for the $\langle 111 \rangle$ direction of the opal lattice. Ensembles of mono-dispersed CdS nano-particles have been synthesized in the porous system of precious opals by a solution technique. Our AFM observation shows a clear image of CdS particles (size of the particle, 5–20 nm) incorporated into the opal. Our Raman spectrum has confirmed the presence of CdS micro-crystals. The results demonstrate that mono-sized CdS crystals may be arranged in ordered arrays of quantum dots as well as quantum wires by controlling the stacking sequence of silica spheres. This type of solids containing ordered nano-sized semiconductor particles may be applied for photo-electronic devices. Future development of this topic is associated with (1) preparation of perfect opal lattices and more regular semiconducting nano-particle lattices and (2) modification of the opal photonic bands by preparing nano-particles with special refraction indices and shapes in the opal voids.

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